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<p>The synthesis and cryogenic solid state photochemistry of poly(4-(2,4,6-tri-<i>tert</i>-butylphenyloxalyl)styrene) is described. Photolysis of the polymer at 77K leads to a strong, broadened electron spin resonance spectrum consistent with formation of phenoxy radicals on the polymer backbone. The ESR signal of the polymeric phenoxy signal is stable at 77K. Thawing of the sample to room temperature leads to unusually high pressure of volatile gases, presumably CO from the photolysis -- indicating fairly good radical generation efficiency. Recooling of the sample to 77K yields a considerably narrowed spectrum -- the residual spectrum in attributable to the stable leaving group radical.</p>					
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Technical Report #18

PROGRESS TOWARD SYNTHESIS
OF POLYMERIC POLYRADICALS

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Progress Report

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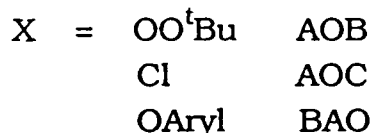
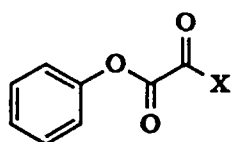
PROGRESS TOWARD SYNTHESIS OF POLYMERIC POLYRADICALS

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ABSTRACT: Attempted synthesis of monomers bearing groups to allow generation of phenoxy moieties is described. In general, such monomers have not been readily isolated. We feel that functionalization of phenolic groups in an existing polymer will be more efficient, as demonstrated by synthesis and irradiation of poly(4-(2,4,6-tri-*tert*-butylphenyloxalyl)styrene). *Keywords: organic chemistry, polymer chemistry, photochemistry, Electrophilic Aromatic Substitution, Radical Chemistry, Photoreactive Materials, Noncovalent Interactions*

INTRODUCTION: In the first two years of this project, this group has invested most of its effort in design and evaluation of leaving groups that would allow thermal and photochemical phenoxy generation in the solid state by unimolecular chemistry. This work resulted in the synthesis of the aryloxyoxalyl *tert*-butylperoxides, aryloxyoxalyl chlorides, and *bis*-aryloxalates (AOB's, AOC's, and BAO's,¹ respectively). With the development of these groups, we were able to

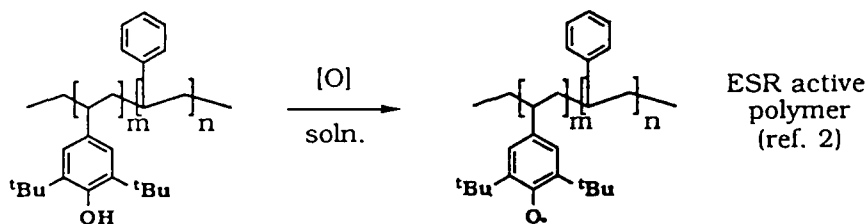
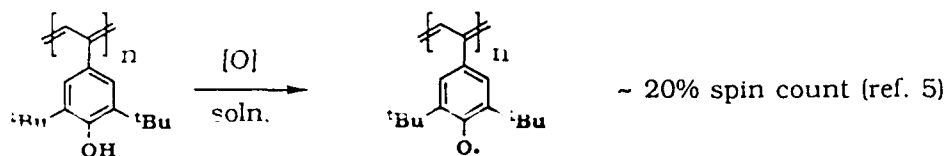


undertake the syntheses of polymers based on this chemistry. Since the project inception, other groups have used different strategies to attempt to make related polymers. We will not explicitly refer to most of these other efforts, but note that our own efforts have been influenced by the chemistry found by others. In particular, we have concentrated on generation of polymers with many, but nonconjugated, radical centers. In general, the synthetic strategies for these tend to be easier than those for the conjugated polymers. Since a variety of efforts by others based upon solution phase generation of conjugated polyradicals have usually led to 20% spin count generation or less, we felt that we would concentrate on equalling or bettering this benchmark for unconjugated polymers, then try to take advantage of the greater stability of radicals in the solid state by generating (at a future time) conjugated polyradicals through use of our solid state photochemistry.

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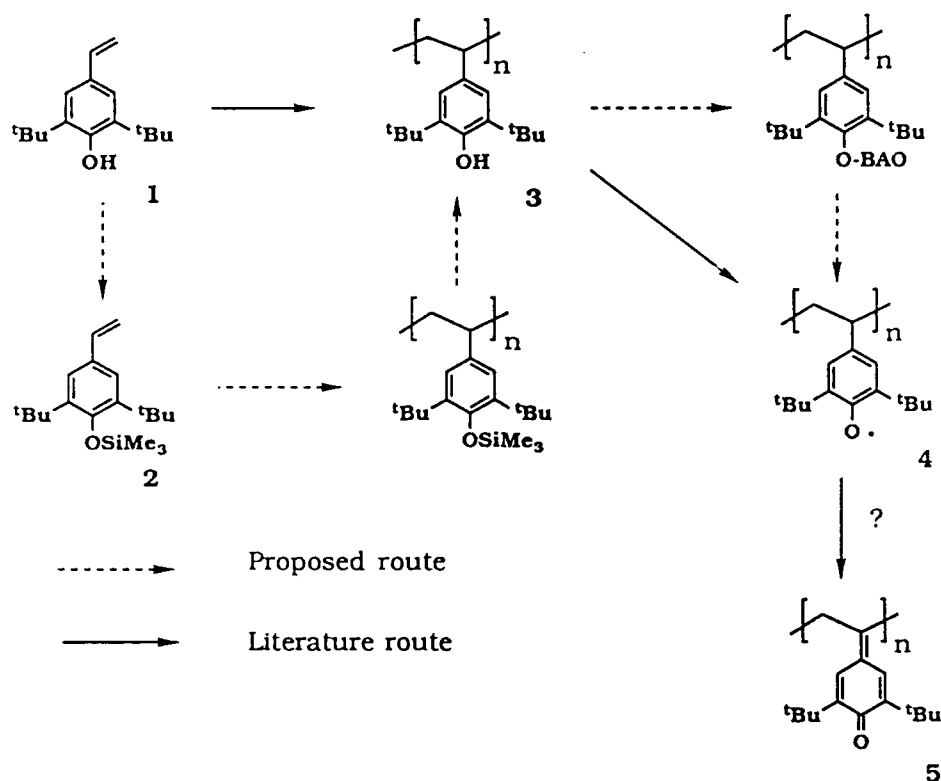
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BACKGROUND: We have concentrated on *tert*-butylated derivatives of poly(4-oxystyrene) and poly(4-oxy-phenylacetylene). The *tert*-butyl groups should lend added stability to radicals in the solid state as well as solution, as shown particularly well by the results described in Technical Report 16. Generation of copolymers of 4-oxy-2,6-di-*tert*-butyl-styrene with styrene by solution

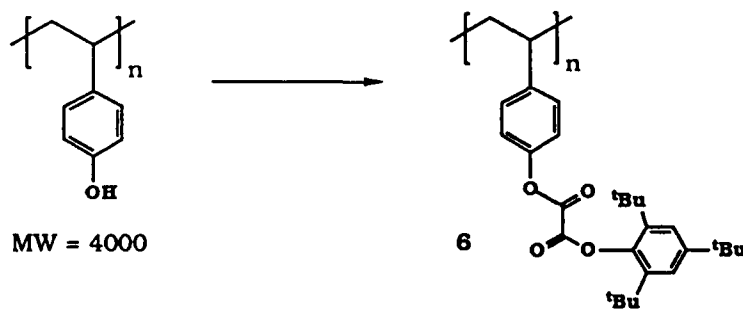


phase oxidation was described in an earlier work², but workers at Exxon³ as well as ourselves have found it difficult to reproduce this work as described. The main difficulties lie with synthesis of the polymeric phenol, as well as with the oxidation step to the polyradical. We and the Exxon workers have found that the described cationic polymerization of **1** to give polymer does not work well in our hands, yielding instead mostly insoluble polymers (see solid arrow route on scheme on following page). Radical-initiated polymerization is also unsatisfactory in the case of unprotected phenolic monomer **1**. Our recent efforts at radical polymerization of protected versions of **1** (e.g., the trimethylsilylated derivative **2**) indicate better polymerization efficiency and product solubility by this route. This work is still in progress (see dashed arrow route on scheme on following page). Even when we overcome this difficulty, we note that the Exxon workers claim that solution phase oxidation of homopolymer **3** leads to poor yields of radicals, attributable to side product oxidative formation in **4** of the quinone groups in **5**. We also have had much difficulty with solution phase oxidation of **3**, and our evidence to date is not inconsistent with the hypothesis of the Exxon workers, in that we obtain oxidation products with yellow colors and little or no ESR active material, despite the reports in the earlier literature.² We feel that synthesis of polymer **3** followed

by functionalization with our BAO or AOB groups (dotted arrow route below) in the solid state may yield a better yield of radicals, but this remains to be established.



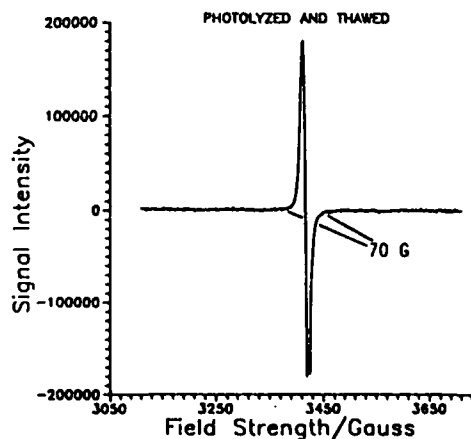
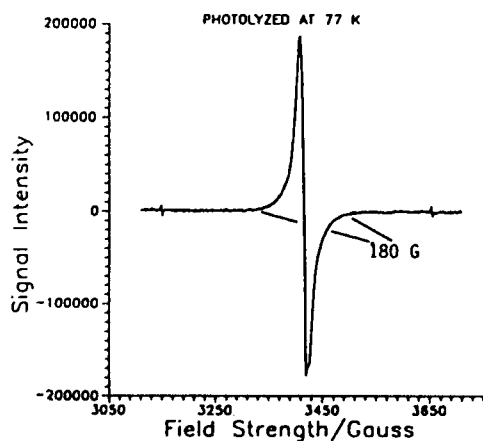
As a result of this, we recently decided to attempt generation of polyradicals without the synthetically difficult (though desirable) 2,6-di-*tert*-butyl stabilization. Technical Report 14⁴ shows that even unstabilized phenoxyl radicals have considerable stability when generated by our solid state photochemical methods in rigid media, well past 77 K. We attempted the straightforward experiment of functionalizing commercially available poly(4-hydroxystyrene) with our thermally stable BAO group to give polymer **6**.



EXPERIMENTAL: Poly(4-hydroxystyrene) of molecular weight 4000 was obtained from Hoesch-Celanese Company and purified by reprecipitation. 2,4,6-Tri-*tert*-butylphenoxyalyl chloride (AOC) was synthesized as described in our earlier work.¹ Polyhydroxystyrene and 2.0 mol-equiv of pyridine was dissolved in 100 mL of dry THF at 0°C under N₂. The AOC was added slowly as a solution in 25 mL of THF, and the reaction stirred overnight. A white precipitate resulted, which was filtered. The organic filtrate was reduced in volume to about 50 mL, then poured into methanol to precipitate the pale yellow polymeric **6** in high yield. The polymer was fully and satisfactorily characterized by IR and NMR spectroscopy.

Electron spin resonance (ESR) experiments were carried out on a Bruker Instruments ESP-300 X-band spectrometer at 9.608 GHz. Samples were sealed under vacuum in quartz ESR tubes and irradiated for 30 min at 77K through liquid nitrogen in a Suprasil ESR dewar (Wilmad Glass Company, Inc.), using a quartz outer filter sleeve with a 1000W Xenon arc lamp at a distance of 4-6 inches. *Care must be taken upon thawing the ESR sample tubes, due to appreciable buildup of gas pressure after the irradiated sample is thawed.*

RESULTS: Photochemical irradiation of powdered polymer **6** turned the polymer yellowish and gave rise quickly to a strong ESR spectrum of typical of phenoxy-type radicals in the solid state, a single, broadened asymmetric peak in the $g = 2.0$ region. This signal mostly disappears upon warming to room temperature and recooling to 77 K, as expected by comparison to the earlier work.⁴ The disappearing broader portion of the spectrum is due to the phenoxy species on the polymer backbone. The residual narrow peak is attributable to the stable 2,4,6-tri-*tert*-butylphenoxy species, by comparison to other spectra of this radical, which has only small broadening due to hyperfine



coupling interactions. The spectrum after initial irradiation looks very similar to that of an unsymmetric monomeric BAO analogs, and acts similarly upon warming. We have not yet been able to evaluate the spin count in this sample, but the amount of generated radical centers must be fairly high, due to the unusually high gas buildup in these photolyses (no other BAO sample gives so much under similar conditions) and the very strong resonance in the ESR spectrum, far stronger than for monomeric BAO's irradiated under similar conditions. The spectrum is shown on the previous page.

FUTURE PROSPECTS: By the above experiment, we should now be able to functionalize phenolic polymers with our BAO group and carry out photochemical development of portions of the polymer samples to become paramagnetic. A variety of polymers and copolymers is limited only by commercial or synthetic availability. In particular, we hope to make efficacious the synthesis of *tert*-butylated phenolic polymers, which should yield radical concentration stable up to room temperature, yielding a room temperature stable paramagnetic material. In collaboration with workers at Clark University who have offered to obtain magnetic susceptibility measurements for us, we intend to evaluate the potential of such polymers as magnetic information storage materials.

[This work is still unpublished, pending the synthesis of other, related polymers to make a more complete story of the generalizability of the chemistry reported herein.]

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